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<b>(54) Title:</b> SLIP-COATED ELASTOMERIC FLEXIBLE ARTICLES AND THEIR METHOD OF MANUFACTURE		
<b>(57) Abstract</b>  In accordance with the present invention, there is provided a flexible article displaying slip properties with respect to damp and dry mammalian tissue without use of powder lubricants. The article is comprised of a substrate layer having an elastomeric material, the substrate layer having a first surface and a second surface, a cross-linked polymer coating, the coating having a third surface and a fourth surface, wherein the third surface of the coating is covalently bonded to the second surface of the substrate layer and, optionally, a damp slip-conferring amount of a lubricant composition applied to the fourth surface of the coating. The coating is non-blocking, exhibits excellent adhesion to the substrate layer even at high elongation values and also exhibits excellent dry slip during, for example, donning of a surgeon's glove. The coating is prepared from a coating composition containing an acrylic-type resin which contains styrene. The lubricant composition confers excellent damp/wet slip during, for example, damp/wet donning of a surgeon's glove. The lubricant composition is selected from the group consisting of a first composition and a second composition. The first composition comprises an acetylenic diol and at least one compound selected from the group consisting of an organo-modified silicone, and amino-modified silicone, and a cationic surfactant. The second composition comprises a cationic surfactant and at least one compound selected from the group consisting of an organo-modified silicone, an amino-modified silicone, and an acetylenic diol. The elastomer may be natural or synthetic, and is preferably selected from the group consisting of natural rubber, a block copolymer, a styrene-isoprene-styrene block copolymer and combination thereof. The cationic surfactant is preferably 1-hexadecylpyridinium chloride monohydrate.		

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SLIP-COATED ELASTOMERIC FLEXIBLE ARTICLES  
AND THEIR METHOD OF MANUFACTURE

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TECHNICAL FIELD OF THE INVENTION

This invention relates to elastomeric flexible articles (e.g., film articles), particularly powder-free medical gloves, that exhibit enhanced lubricity ("slip") with respect to both dry and damp surfaces, particularly skin or other tissue of the wearer, as compared to similar articles or films that are not treated as described herein. This invention also relates to a process for making such articles. This invention further relates to a method of treating elastomeric flexible articles with a slip coating and optionally further treating with a lubricant composition.

BACKGROUND OF THE INVENTION

Elastomeric surfaces of articles, in general, exhibit poor lubricity with respect to a dry surface, such as dry skin or other mammalian tissue. These properties are due to surface friction. Additionally, many elastomeric articles or surfaces display poor lubricity with respect to damp surfaces. A high coefficient of friction is a distinct disadvantage in those applications where an elastomeric surface must slide on another surface, such as in the donning of gloves over dry or damp skin. This is particularly important in the use of medical gloves, such as examination gloves and surgeon's glove. These gloves are relatively close fitting in order to provide sensitivity. Further, most surgeons don their gloves after scrubbing up and without having fully dried their hands, so that their hands may be distinctly damp. Accordingly, the

5 elastomeric materials useful in such applications must exhibit enhanced lubricity with respect to dry surfaces ("dry slip"), enhanced lubricity with respect to damp surfaces ("damp slip"), and the requisite mechanical properties. The prior art has attempted various ways to  
10 produce powderless gloves which satisfy these requirements.

One prior approach is to halogenate the surface of rubber gloves with chlorine or bromine to make it slippery, i.e., reducing tackiness and decreasing the  
15 coefficient of friction of the rubber gloves. In the case of chlorine as the halogen, the prior art discloses the production and use of chlorinated water to treat the rubber gloves. Such methods include (1) direct injection of chlorine gas into the water mixture, (2) mixing high  
20 density bleaching powder and aluminum chloride in water, (3) brine electrolysis to produce chlorinated water, and (4) acidified bleach. See for example U.S. Pat. Nos. 3,411,982 (Kavalir), 3,740,262 (Agostinelli), 3,992,221 (Homsy, et al.; treating outer surface with chlorine  
25 gas), 4,597,108 (Momose), and 4,851,266 (Momose). However, chlorination produces surfaces which have very poor damp slip.

There are other prior rubber gloves having a slip layer bonded to the inner surface of such gloves.  
30 Examples of gloves which have an inner layer of elastomeric material with particulate lubricant imbedded therein are disclosed in U.S. Pat. Nos. 4,070,713 (Stockum), 4,143,109 (Stockum), 5,284,607 (Chen) and 5,395,666 (Brindle; together with a surfactant, but ionic  
35 surfactants are not recommended), and which disclose surgeon's gloves with various polymeric slip coatings bonded to the inner surface thereof are U.S. Pat. Nos. 3,286,011 and 3,411,982 (both to Kavalir et al.; an inner layer of a rubber/resin combination, wherein the resin  
40 maybe acrylic-type resins, allowing elongation values of

5 200% to 700%); 3,813,695 (Podell, et al.; an inner layer  
of hydrophilic plastic material, e.g., hydrogel polymer),  
3,856,561 (Esemplare, et al.; an inner layer of a  
copolymer of vinyl or vinylidene chloride and an alkyl  
10 acrylate, e.g., copolymer of vinyl chloride or vinylidene  
chloride with butyl acrylate and acrylic acid),  
4,302,852 (Joung; e.g., inner layer of silicone),  
4,482,577 (Goldstein, et al.; elastomeric article is  
cleaned, immersed in a concentrated solution of a strong  
acid, washed, dipped in a solution of an uncured  
15 hydrophilic polymer and then cured; articles are  
described as stretchable to 700%), 4,499,154 (James, et  
al.; article is pre-treated in a dilute acid solution  
prior to applying inner layer; uses specific hydrogel  
polymers as the inner layer which is then treated with a  
20 cationic surfactant or fatty amine) and 4,575,476  
(Podell, et al.; hydrogel polymer inner layer treated  
with cationic, anionic or nonionic surfactant).

Some of the latter-type gloves experience  
delamination of the layers or produce a "cobblestoning"  
25 effect when stretched, for example, when the gloves are  
donned. Prior gloves have been made to address this  
problem. According to U.S. 5,570,475, prior attempts to  
improve resistance to delamination have included  
treatment of the natural or synthetic elastomeric base  
30 material by an acid priming step and a neutralizing step  
prior to the polymer coating step, citing U.S. 4,499,154  
(noted above). According to U.S. 4,548,844 (Podell et  
al.), a trivalent cationic salt, e.g., aluminum salt, may  
be applied to the elastomeric article prior to or  
35 simultaneously with the application of the hydrophilic  
hydrogel polymer so as to provide for improved adhesion  
of the polymer to the article after curing. Others  
gloves utilize certain types of polymers as the inner  
layer to avoid or minimize delamination when the article  
40 is stretched or flexed. For example, U.S. 4,082,862

5 (Esemplare et al.) is identified as an improvement over  
U.S. 3,856,561 (Esemplare et al.) to avoid the  
"cobblestoning" effect observed when the elastomeric  
article is stretched to a large extent, e.g., over 450%.  
Therein, a blend of polymers each with specific required  
10 properties is used. As another example, U.S. 5,570,475  
(Nile et al.) discloses copolymers of styrene or ethylene  
with half esters of maleic acid.

The foregoing differ from the present invention.

15 SUMMARY OF THE INVENTION

In accordance with the present invention, there is  
provided a flexible article displaying slip properties  
with respect to damp and dry mammalian tissue without use  
of powder lubricants. The article is comprised of a  
20 substrate layer having an elastomeric material, the  
substrate layer having a first surface and a second  
surface, a crosslinked polymer coating, the coating  
having a third surface and a fourth surface, wherein the  
third surface of the coating is covalently bonded to the  
25 second surface of the substrate layer and, optionally, a  
damp slip-conferring amount of a lubricant composition  
applied to the fourth surface of the coating. The  
coating is non-blocking, exhibits excellent adhesion to  
the substrate layer even at high elongation values and  
30 also exhibits excellent dry slip during, for example,  
donning of a surgeon's glove. The lubricant composition  
confers excellent damp/wet slip during, for example,  
damp/wet donning of a surgeon's glove.

There is also provided a method of treating an  
35 elastomeric flexible article. The method involved in  
producing the coated elastomeric articles is a multistep  
procedure which includes (1) forming an elastomeric  
article, (2) priming the surface of the elastomer with an  
acidic solution, (3) coating the elastomer surface with a  
40 non-blocking, slip-conferring polymer solution, (4)

5 curing the elastomer and the polymer, (5) chlorinating at  
least the wearer-contacting surface of the coated  
article, (6) neutralizing the article surface and  
residual chlorine, and, optionally, (7) treating the  
wearer-contacting surface with a lubricant composition to  
10 enhance the damp/wet slip properties thereof.

An important feature of this invention is that the  
slip coating exhibits tremendous adhesion to elastomeric  
substrates even when such substrates are elongated to  
break. These coatings are prepared from a coating bath  
15 composition containing (1) an acrylic-type resin which  
may contain reactive functional groups such as carboxyl,  
hydroxyl, amide and methylol groups and which may be a  
copolymer made using styrene, acrylonitrile and/or an  
alkylene monomer and which may be self-reactive (i.e.,  
20 that a crosslinker is not required for crosslinking  
thereof); (2) a metal salt; (3) an acid catalyst; and (4)  
a highly reactive crosslinking agent (which is optional  
if the resin is self reactive). The acrylic-type resins  
contain adequate functionality when combined with an  
25 effective amount of the crosslinking agent (unless the  
resin is self-reactive, then an effective amount of  
reactive functional groups) to effect curing thereof.  
The crosslinkers employed in this invention are typically  
reactive toward thiol, carboxyl, amide, and hydroxyl  
30 groups. The metal salt also acts as a coagulant for the  
resin thus resulting in an effective deposition of the  
coating onto the elastomeric substrate. The crosslinking  
of the coating also results in either immobilizing or  
creating a barrier to the migration of the proteins and  
35 curatives in the elastomeric substrate which can  
sometimes be allergenic. Such materials are typically  
leached out by the users sweat, but since the coating is  
water resistant, the sweat is prevented or at least  
inhibited from leaching such components from the  
40 elastomeric substrate.

5           The slip coating provided by the present invention  
has excellent characteristics of slipperiness. A simple  
way to demonstrate the slipperiness of this coating is to  
place two coated rubber surfaces together and rub the  
contacting surfaces back and forth while grasped between  
10 the fingers. Previous slip coatings which have been  
tested do not slip at all or with difficulty when held in  
this manner. However, the coatings provided by the  
present invention readily slip irrespective of the amount  
of grasping pressure applied.

15           The coatings produced by the present invention are  
highly durable and water resistant. This is a desirable  
feature since elastomeric articles, specifically natural  
rubber latex medical devices, may be subjected to  
rigorous washing and autoclaving steps to remove the  
20 allergenic constituents from the articles. The articles  
may also be subjected to a chlorination step. The  
coatings provided by the present invention are unaffected  
by such treatments.

          The elastomeric articles of the present invention  
25 are provided with a non-blocking surface thus eliminating  
the need for application of a post-cure powder slurry as  
is commonly employed on conventional elastomeric  
articles. Furthermore, the coating may be formulated  
from a variety of commercially available water-based  
30 acrylics including styrene acrylics or acrylic  
acrylonitrile lattices. These lattices are applied to  
the elastomeric articles as an aqueous resin containing a  
water-soluble crosslinking agent such as a melamine,  
urea-formaldehyde, or glycoluridil commercial  
35 crosslinker. The use of water-based commercially  
available materials is an advantage since this leads to  
reduced manufacturing costs, low VOCs (volatile organic  
compounds), and increased worker safety.

          The elastomer of the substrate layer can be either a  
40 natural or a synthetic elastomer, or a combination



5    thereof. The elastomer is preferably selected from the  
group consisting of natural rubber, a polyurethane, a  
homopolymer of a conjugated diene, a copolymer of at  
least two conjugated dienes, a copolymer of at least one  
conjugated diene and at least one vinyl monomer and  
10   combinations thereof. The conjugated diene may contain  
hetero atoms, such as conjugated dienes which have been  
halogenated, e.g., chloroprene. Preferred conjugated  
dienes include butadiene, isoprene, piperylene and  
chloroprene. Preferred vinyl monomers include alkenyl  
15   arenes, e.g., styrene; alkylenes, e.g., ethylene and  
propylene; and acrylonitrile. The term "combinations  
thereof" in regard to the elastomer includes physical  
combinations thereof in a single layer and layered  
combinations thereof, for example, a multi-layered  
20   elastomeric article having a layer of polyurethane formed  
over and adhering to a layer of natural rubber.

          The lubricant composition has a silicone surfactant  
and at least one organic surfactant. The silicone  
surfactant may be a non-modified or modified silicone.  
25   The organic surfactant may be any such surfactant  
compatible with the silicone surfactant. Preferably, the  
organic surfactant is a cationic surfactant, e.g., 1-  
hexadecylpyridinium chloride monohydrate (also known as  
cetylpyridinium chloride or CPC).

30           In one embodiment, the article is a surgeon's glove.  
Medical powder-free gloves having the cured resin coating  
have good dry donning and resistant to delamination, and  
if further treated with the lubricant composition provide  
superior lubricity with respect to wet/damp donning in  
35   comparison to the current chlorinated surgical gloves in  
the market.

## 5 DETAILED DESCRIPTION OF THE INVENTION

The invention envisages flexible elastomeric articles including those adapted for use in partial or total contact with mammalian tissue, such as surgical, examination and dental gloves, condoms, bandages, catheters, ureters, sheathes and sheath-type incontinence devices and other film articles. Additionally, the damp/dry slip-conferring materials may be provided on one or more surfaces of the article including, but not limited to, an inner and/or outer surface relative to the wearer, as appropriate under the circumstances of the use of each article.

For purposes of this description, the outer surface of an article and, in particular, a glove, is defined as that surface which becomes an external surface of the glove in the position of actual use when worn. The inner surface is defined as that surface which is adjacent to the skin of the wearer when worn. The reverse is true in the case of a catheter or ureter: the outer surface is the surface in contact with the wearer's tissue. To avoid ambiguity, the term "wearer-contacting surface" will be used herein. "Tissue" includes skin or epithelia without limitation.

The elastomer used in the substrate layer may be a natural or synthetic rubber. Without limitation, synthetic rubbers include polyurethane, a homopolymer of a conjugated diene, a copolymer of at least two conjugated dienes, a copolymer of at least one conjugated diene and at least one vinyl monomer, and combinations thereof.

The conjugated dienes are preferably ones containing from 4 to 8 carbon atoms. Examples of such suitable conjugated dienes include: 1,3-butadiene (butadiene), 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene (piperylene), 1,3-hexadiene, and the like. The conjugated dienes may contain hetero

5 atoms. Such conjugated dienes include those which have been halogenated, for example, chloroprene. Mixtures of such conjugated dienes may also be used. The preferred conjugated dienes are butadiene, isoprene and chloroprene.

10 Any vinyl monomer may be used for copolymerization with at least one conjugated diene to prepare synthetic rubbers so long as the resulting copolymer is elastomeric. Without limitation, such vinyl monomers include alkylenes, alkenyl arenes, and acrylonitrile.

15 The preferred alkylenes are ethylene, propylene and butylenes. The preferred alkenyl arenes are monoalkenyl arenes. The term "monoalkenyl arene" will be taken to include particularly those of the benzene series such as styrene and its analogs and homologs including o-

20 methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene, alpha-methylstyrene and other ring alkylated styrenes, particularly ring-methylated styrenes, and other monoalkenyl polycyclic aromatic compounds such as vinyl naphthalene, vinyl anthracene and

25 the like. The preferred monoalkenyl arenes are monovinyl monocyclic arenes such as styrene and alpha-methylstyrene, and styrene is particularly preferred.

The copolymers may be random, tapered or block copolymers. If the copolymers are block copolymers, it

30 will be understood that each of the blocks thereof may be a homopolymer, a random copolymer or a tapered copolymer as long as each block predominates in at least one class of the monomers characterizing the block. For example, blocks of alkenyl arenes may comprise styrene/alpha-

35 methylstyrene copolymer blocks or styrene/butadiene random or tapered copolymer blocks as long as the blocks individually predominate in alkenyl arenes.

Preferred rubbers are natural rubber and synthetic rubbers, including polyurethane, neoprene, nitrile

40 rubber, block copolymers of styrene and butadiene,

5 particularly a styrene-butadiene-styrene block copolymer,  
and block copolymers of styrene and isoprene,  
particularly a styrene-isoprene-styrene block copolymer.

Natural rubber and polyurethane are more preferred, with  
natural rubber being most preferred. Neoprene is a  
10 homopolymer of the conjugated diene chloroprene. Nitrile  
rubber is a copolymer of the conjugated diene butadiene  
and the vinyl monomer acrylonitrile.

The block copolymers of alkenyl arenes ("A" blocks)  
and conjugated dienes ("B" blocks) are preferably network  
15 forming, i.e., at least two A blocks and at least one  
B block. The simplest form of such a block copolymer is  
A-B-A, which is a triblock copolymer. In such a  
synthetic rubber, the A blocks are thermodynamically  
incompatible with the B block(s) resulting in a rubber  
20 consisting of two phases; a continuous elastomeric phase  
(B blocks) and a basically discontinuous hard, glass-like  
plastic phase (A blocks) called domains. These domains  
act as physical crosslinks anchoring the ends of many  
block copolymer chains. Since the A-B-A block copolymers  
25 have two A blocks separated by a B block, domain  
formation results in effectively locking the B blocks and  
their inherent entanglements in place by the A blocks and  
forming a network structure. Such a phenomenon allows  
the A-B-A rubber to behave like a conventionally  
30 vulcanized rubber that contains dispersed reactive filler  
particles. These thermoplastic A-B-A rubbers are  
physically crosslinked by the domains in a network  
structure as opposed to being chemically crosslinked like  
a conventionally vulcanized rubber. As such, these  
35 polymers may be handled in thermoplastic forming  
equipment and are soluble in a variety of relatively low  
cost solvents. Additionally, when polymers of this type  
are used, the vulcanization step may be eliminated and,  
contrary to vulcanized scrap rubbers, the scrap from the  
40 processing of these thermoplastic elastomers can be

5 recycled for further use.

The block copolymers may be produced by any well known block polymerization or copolymerization procedures including the well known sequential addition of monomer techniques, incremental addition of monomer technique or  
10 coupling technique as illustrated in, for example, U.S. Pat. Nos. 3,251,905; 3,390,207, 3,598,887 and 4,219,627, the disclosures of which are incorporated herein by reference. As is well known in the block copolymer art, tapered copolymer blocks can be incorporated in the  
15 multiblock copolymer by copolymerizing a mixture of conjugated diene and alkenyl arene monomers utilizing the difference in their copolymerization reactivity rates. Various patents describe the preparation of multiblock copolymers containing tapered copolymer blocks including  
20 U.S. Pat. Nos. 3,251,905; 3,265,765; 3,639,521 and 4,208,356, the disclosures of which are incorporated herein by reference.

It should be observed that the above-described polymers and copolymers may, if desired, be readily  
25 prepared by the methods set forth above. However, since many of these polymers and copolymers are commercially available, for example, KRATON™ polymers available from Shell Oil Company, it is usually preferred to employ the commercially available polymer as this serves to reduce  
30 the number of processing steps involved in the overall process.

Typical thicknesses of the elastomeric substrate layer for surgical gloves range from about 15 to about 400 microns, preferably from about 100 to about 350  
35 microns. Surgical gloves tend to be about 150 microns thick and orthopedic gloves tend to be about 300 microns thick.

To confer both dry and damp slip to the coated elastomeric article, the substrate is treated using a

- 5 multiple step process involving (1) coating with an acrylic-type resin coating solution, (2) curing the coating and substrate, (3) chlorinating the article, and (4) surfactant treating the article with a lubricant composition containing a silicone and organic
- 10 surfactants. The resultant elastomeric products are powderfree and highly lubricious.

The elastomeric surface may be prepared prior to coating in a priming step by acid treating or other surface preparation techniques in order to insure

15 excellent adhesion between the coating and the elastomeric substrate. Polymer surfaces are often difficult to bond to because of low surface energy, contamination, and the bloom of plasticizers or low molecular weight compounds. Other methods of preparing

20 the elastomeric surface may include but is not limited to plasma treatment, corona treatment, ozone treatment, or chemical priming of the elastomer. The coating system exhibits excellent adhesion even when the elastomeric article is highly elongated.

## 5 ACID PRETREATMENT STEP ALTERNATIVE METHODS

By way of example, gloves according to the present invention have been prepared gloves using two distinct acid surface preparation techniques including treating the latex with a 2% sulfuric acid predip prior to rinse  
10 and overcoating with the coating solution. An alternate method of surface preparation involved acidification of the leach prior to overcoating. To the leach water was added about 0.25% by weight of concentrated sulfuric acid and the gloves were placed in the leach tank for about  
15 twelve minutes at about 110°F. Both procedures produced gloves that have coatings with excellent adhesion. The excellent adhesion of the coating was evident when the coated latex article was elongated four hundred percent (400%) and no delamination of the coating occurred.

20 As has been discussed, the coating has an acrylic type resin, crosslinking agent, metal salt and an acid catalyst. The following is a discussion of the preferred embodiments pertaining to each of the aforementioned components.

25 A number of acrylic emulsions or dispersions have been found suitable in producing highly adherent coating surfaces on the elastomeric articles. The acrylic emulsions evaluated contain residual unreacted groups such as carboxyl or hydroxyl. Suitable acrylic resins,  
30 the styrene-acrylic resins, or acrylonitrile-modified acrylics resins NP-32 and Rhoplex® AC-3094, AC-2573, and AC-1024 available from Rohm and Haas Co., Philadelphia, PA; Carboset® 531 and Carboset® GA-1594, available from B.F. Goodrich Speciality Chemicals, Cleveland, Ohio; and  
35 UCAR® Latex 413, and UCAR Latex 452 available from UCAR Emulsion Systems, Union Carbide Corp., Cary, N.C.

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PRODUCT	FUNCTIONALITY	SURFACTANT SYSTEM	COMPOSITION
ROHM & HAAS NP-32	carboxyl	nonionic	46% solids; self-crosslinking acrylic emulsion
ROHM & HAAS AC-3094	carboxyl and hydroxyl	nonionic	47% solids; acrylic emulsion
ROHM & HAAS AC-2573	carboxyl	nonionic	46% solids; acrylic emulsion
ROHM & HAAS AC-1024	carboxyl and hydroxyl	nonionic and anionic	50% solids; styrene acrylic copolymer
CARBOSET® 531	carboxyl	not available	25% solids; self-crosslinking styrene acrylic copolymer
CARBOSET® GA-1594	carboxyl	not available	40% solids; styrene acrylic copolymer
UCAR® 452 (styrene-acrylic latex)	hydroxyl and carboxyl	nonionic, Nonyl phenoxy poly(ethyleneoxy) ethanol	44% solids; copolymer of butyl acrylate, acrylonitrile and methacrylic acid (CAS #27401-61-2) and copolymer of styrene, ethyl acrylate, methacrylic acid, and hydroxyethylacrylate (CAS #29828-29-3)
UCAR® 413	carboxyl	nonionic, nonylphenoxy poly(ethyleneoxy) ethanol (CAS	47% solids; copolymer of butyl acrylate, methyl



		#9016-45-9)	methacrylate, and methacrylic acid (CAS #25035-69-2)
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The specific compositions of the Rohm & Haas, UCAR®, and Carboaset® acrylic copolymer products are considered proprietary. Most suitable monomers for these emulsion products exhibit low water solubility. Other monomers

10 such as methacrylic acids and acrylic acids may be included to improve the adhesion characteristics of these emulsions. Available surfactants used for these emulsions are anionic, cationic, and nonionic. Mixed anionic and nonionic surfactants are the most commonly used in

15 acrylic emulsions. Cationic surfactants are rarely used however when used they are the quaternary ammonium halide salt type. Typical constituents in acrylic copolymer emulsions are given below:

20 Anionic Surfactants

Stearate Soaps

Dodecyl benzene sulphonate

Sodium Dioctyl sulphosuccinate

25 Cationic Surfactants

Cetyl trimethyl ammonium bromide

Nonionic Surfactants

Polyethoxylated nonyl phenol

30 Polyethoxylated polypropylene glycol

Emulsion polymers are two phase systems of two immisible liquids, small droplets of polymer are the dispersed phase and water is the continuous phase. It

35 is believed that while monomers can combine during polymerization in a variety of configurations including

5 random, block, alternating and graft the vast majority of  
these acrylic polymers that are used in coatings are  
random. The random configuration decreases tenacity and  
crystallization not desirable in acrylic copolymer  
coating polymers. Self crosslinking of these emulsions  
10 can be accomplished by incorporating an acrylamide or an  
alkoxy methyl acrylamide into the polymer backbone. The  
acrylamide modified acrylics require a baking schedule of  
approximately 20 to 30 minutes at 150-180°C.  
The preferred crosslinkers are the melamines which may be  
15 polymeric or monomeric and methylated or non-methylated.  
Suitable melamines that functioned effectively as  
crosslinkers and commercially available were the Cymel®  
373, Cymel® 350, and Cymel® 303 available from Cytec  
Industries, West Patterson, N.J., and the Astro  
20 Industries Aricel PC-5, and Monsanto's Resimine® 797.  
Glycoluridil crosslinkers may also be used in the present  
invention, for example, Cymel® 1171 and 1172 available  
from Cytec Industries, West Patterson, N.J. produced  
excellent coatings on the elastomeric substrates. Urea-  
25 formaldehydes were found to effectively function as  
crosslinkers, for example, the Beetle Resins such as  
Beetle® 65 was found effective.

5 **CROSSLINKER CHARACTERIZATION**

TYPE	METHYLATED MELAMINE (CYMEL® 373, Resimine 797, AND CYMEL® 350)	METHYLATED UREA FORMALDEHYDE (BEETLE 65)	GLYCOURILS (CYMEL® 1172) AND (CYMEL 1171)	MELAMINES FULLY ALKYLATED (CYMEL® 300 AND 303) Aricel® PC-5
REACTIVE WITH :				
HYDROXY GROUPS	YES	YES	YES	YES
CARBOXYL GROUPS	YES	SLIGHT	YES	YES
AMIDE GROUPS	YES	YES	YES	YES
TYPICAL CURE TEMPERATURES	ELEVATED TEMPERATURE (250°F)	ROOM TEMPERATURE	ELEVATED TEMPERATURE (200 °F)	ELEVATED TEMPERATURE (45°C)
CATALYST NEEDED	LIKELY	NO	YES	YES

One function of the metal salt is to serve as a  
 10 coagulant which is in part responsible for the remarkable  
 adhesion observed for the coating. The aluminum nitrate  
 acts as a coagulant for the latex and as a catalyst for  
 the crosslinking of the melamine. A number of metal salt  
 catalysts exist that fulfill the requirements described  
 15 in the present invention. Amongst these are magnesium  
 bromide, aluminum sulfate, aluminum nitrate, zinc  
 nitrate, magnesium nitrate, silver nitrate, and zirconium  
 complexes. The metal nitrates are preferred due to their  
 excellent water solubility.

20 A number of acid catalysts were evaluated in the  
 formulations to insure complete curing of the acrylic  
 coatings within the temperature and time constraints of  
 the elastomeric articles. The catalysts evaluated were as  
 follows: Cycat® 4040, Cycat® 600, Phosphoric acid,  
 25 Nacure® 1419, Nacure® 1953, and Nacure® 3525. The

5 catalyst are chemically described as para-toulenesulfonic acid, blocked para-toulenesulfonic acids, and concentrated phosphoric acid. The catalyst are used at very low levels in our formulation as described in the detailed examples.

10 The concentrations of the acid catalysts used in the examples are preferably from 0.001% to 10 percent and most preferably from 0.001% to 3%. The metal salts in the formulations are used preferably at a level from 0.1% to 8% and most preferably from 0.1% to 5%. The total solids  
15 in the formulations preferably range from 1% to 40% and most preferably from 1% to 25%. The crosslinkers in the formulations range preferably from 0% to 25% and most preferably from 0% to 20%.

Preferred cationic surfactants are quaternary  
20 ammonium compounds having at least one C8-C20 hydrocarbyl (alkyl, aryl, aralkyl, or cycloalkyl) group; a preferred hydrocarbyl group is a hexadecyl group. The hydrocarbyl functionality may be attached to a quaternary nitrogen atom that is part of a heterocyclic ring system  
25 (such as a pyridine, morpholine, or imidazoline ring). A variety of other preferred alternative cationic surfactants are listed as follows: benzalkonium chloride, hexadecyltrimethylammonium chloride, hexadecyl pyridinium chloride, stearyl trimethyl ammonium chloride,  
30 dodecylpyridinium chloride, as well as the corresponding bromides, and a hydroxyethylheptadecylimidazolium halide.

Some other preferred surfactants are glycerol stearates, glycerol oleates, cocoaminopropyl betaine, and polyethylene glycol monostearates. Polyethylene glycols  
35 and polyoxypropylene glycols are suitable nonionic surfactants. Also nonylphenol ethoxylates, as well as other ethoxylated acetylenic diols will perform well. Surfactants which contain both polyoxyethylene and polyoxypropylene chains such as the Pluronics® would  
40 prove effective for our invention.

5           A small amount of an anionic surfactant may be added  
to improve the initial response of the elastomer surface  
during the damp donning process. A preferred anionic  
surfactant would be sodium naphthalene sulfonate;  
alternatives include alkyl benzene sulfonates. Special  
10 groups of surfactants such as the sulfonated non-ionic  
polyoxyethylene ethers, sodium dodecyl sulfate,  
sulphosuccinates, phosphate esters, and sodium dodecyl  
benzene sulfonate would also prove effective for our  
invention.

15           The silicone surfactants employed in the present  
invention are principally polyether modified  
polydimethylsiloxanes. Examples of such useful silicones  
are available from OSi Specialties and Dow Corning  
Corporation. The OSi silicones that were evaluated were  
20 from both the NuWet® and SilWet® product lines. NuWet®  
100, 300, and 500 were tested. The preferred SilWet®  
products were SilWet® 7001 and SilWet® 7605. The Dow  
Corning silicone we examined in the present invention was  
Dow Corning 365, an aminomodified silicone. Other  
25 silicones which would prove effective in the present  
invention include dimethicone cyclodimethicone (Dow  
Corning® 245). Also a variety of Silicone based  
quaternary compounds (Tegopren®) that are available from  
Goldschmidt would prove effective in the present  
30 invention.

#### ANCILLARY INFORMATION ON SILICONE SURFACTANTS

          Among the silicone surfactants that would prove  
useful in the invention are included NuWet® 300 and  
35 NuWet® 500, both believed to be polyether modified  
silicones. Also the diquaternary polydimethylsiloxanes  
Tegopren® 6920 and 6922 have proved useful in our  
invention. Also the Silwet® 7605 that is also believed  
to be a polyether modified polydimethylsiloxane has proved

5 quite efficient as a silicone surfactant. Another  
silicone surfactant of use is Dow Corning® 245 that is  
chemically identified as a decamethylcyclopentasiloxane.

To impart damp slip properties to the flexible  
elastomeric article, which is at least substantially  
10 powderless and is preferably chlorinated, the article is  
treated with a lubrication composition. Two preferred  
combinations of components are as follows. The first  
composition comprises (i.e., having at least) (1) an  
acetylenic diol and (2) at least one compound selected  
15 from the group consisting of an organo-modified silicone,  
an amino-modified silicone, and a cationic surfactant,  
preferably, 1-hexadecylpyridinium chloride monohydrate.  
The second composition comprises (1) a cationic  
surfactant, preferably 1-hexadecylpyridinium chloride  
20 monohydrate, and (2) at least one compound selected from  
the group consisting of an organo-modified silicone, an  
amino-modified silicone, and an acetylenic diol. The  
lubricant composition is preferably an aqueous solution  
or dispersion.

25 The compound 1-hexadecylpyridinium chloride  
monohydrate (CAS No. 6004-24-6) is a commercially  
available cationic surfactant. Other suitable cationic  
surfactants include those comprising at least one  
lipophilic moiety such as an alkyl, aralkyl, aryl, or  
30 cycloalkyl group containing 6 to 18 carbon atoms, and a  
hydrophilic moiety such as a substituted ammonium group  
(for example, a tetra-alkylammonium, pyridinium, or like  
group). The counter-ion present should be compatible  
with the tissue of the wearer; it could be, for example,  
35 chloride or other halide.

Preferred cationic surfactants are quaternary  
ammonium compounds having at least one C<sub>6</sub>-C<sub>18</sub> hydrocarbyl  
(alkyl, aryl, aralkyl or cycloalkyl) group; a preferred  
hydrocarbyl group is a hexadecyl group. The hydrocarbyl  
40 group may be attached to a quaternary nitrogen atom which

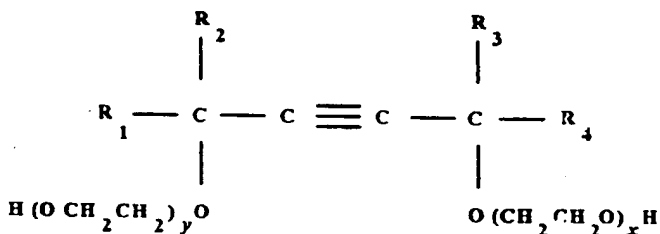
5 is part of a heterocyclic ring (such as a pyridine, morpholine, or imidazoline ring).

As previously mentioned, a particularly preferred surfactant is hexadecylpyridinium chloride. Other suitable cationic surfactants include benzalkonium chlorides, hexadecyltrimethylammonium chloride, 10 dodecylpyridinium chloride, the corresponding bromides, a hydroxyethylheptadecylimidazolium halide, coconut alkyl dimethylammonium betaine and coco aminopropyl betaine.

15 Mixtures of surfactants may also be used.

The cationic surfactant, e.g., the preferred cetylpyridinium chloride, concentration is in the range from about 0.05% to about 2.5% by weight. A range from about 0.25% to about 1.50% by weight, for example, 0.5%, 20 cetylpyridinium chloride solution is preferred.

The acetylenic diols useful in the present invention are acetylenic tertiary glycols and the ethylene oxide adducts of acetylenic tertiary glycols. Preferably, the acetylenic diols used in the practice of the invention



25 are structurally represented by the formula:

in which  $R_1$  and  $R_4$  are alkyl radicals containing from 3-10 carbon atoms, and  $R_2$  and  $R_3$  are selected from the group consisting of methyl and ethyl, and  $x$  and  $y$  have a sum in the range of 0-60, inclusive, where  $y=x=0$

30 represents the acetylenic tertiary glycols. In the preferred case,  $R_1$  and  $R_4$  are alkyl radicals having 3-

5 4 carbon atoms each and  $R_2$  and  $R_3$  are methyl groups.  
Further examples and synthesis techniques for the  
manufacture of these acetylenic diols are disclosed in  
U.S. Pat. Nos. 3,268,593 (Carpenter et al.) and 3,293,191  
(Carpenter et al.), which are hereby incorporated by  
10 reference.

Acetylenic diols useful in the present invention  
preferably have a 10-carbon chain as a backbone with a  
carbon-carbon triple bond in the middle with a hydroxyl  
group on the carbon atoms on either side of the triple  
15 bond. The combination of these groups yields a region of  
high electron density, making the molecule polar. There  
is also a symmetrical, highly branched group on each side  
of this region supplying the molecule with two  
hydrophobic areas. Overall the molecule has a  
20 hydrophobic-hydrophilic-hydrophobic structure, making it  
a good wetting agent or surface tension reducer. See J.  
Schwartz et al., "Acetylenic diol-based additives help  
glove makers meet quality standards," Elastomerics, pages  
16-18, December 1989. Suitable acetylenic diols include  
25 the following available from Air Products and Chemicals,  
Inc., Allentown, PA: Surfynol® 104 (2,4,7,9-tetramethyl-  
5-decyn-4,7-diol), Surfynol® 104E (Surfynol® 104/ethylene  
glycol, 50/50), Surfynol® 440 (Surfynol® 104 + 3.5 moles  
ethylene oxide), Surfynol® 465 (Surfynol® 104 + 10 moles  
30 ethylene oxide) and Dynol® 604 (a mixture of ethoxylated  
acetylenic diols).

The acetylenic diols are preferably ethoxylated  
acetylenic diols such as Dynol® 604 and Surfynol® 400  
series available from Air Products and Chemical Inc.,  
35 Allentown, Pennsylvania. Dynol® 604 is preferred because  
it provides better lubricity. The acetylenic diol is  
used in the form of a solution, such as an aqueous  
solution containing at least 0.01% by weight up to, for  
example, 2% by weight of acetylenic diols. The  
40 acetylenic diols may be used in a mixture or combination.



5           The modified silicones useful in the present  
invention are hydrophilic, nonionic silicones. Examples  
of such silicones are commercially available from OSI  
Specialties, Inc., Danbury, Connecticut are NuWet® 100,  
NuWet® 300 and NuWet® 500. NuWet® 100 is a copolymer  
10 described as an organo-modified polydimethylsiloxane,  
more specifically a polyalkylene oxide modified  
polydimethylsiloxane. NuWet® 300 is also a copolymer  
described as an amino-modified silicone-polyether  
copolymer. As a result of the amino-modification, this  
15 material has reportable quantities of an alkanolamine.  
NuWet® 500 is a blend of an organo-modified  
polydimethylsiloxane (>65%) and an ethoxylated alkyl  
(<20%). There are reportable quantities of ethylene  
oxide (<20%; upper bound concentration per MSD Sheet is  
20 0.0002%). The following Table provides some physical  
properties for these three materials.

5

Physical Property	NuWet® 100	NuWet® 300	NuWet® 500
Appearance	Clear	Clear - Sl. Haze	Clear
Color	Lt. Straw	Lt. Straw to Tan	Colorless to Lt. Straw
Nominal Viscosity, cP	425	3500	400
Solubility in Water	Soluble	Dispersable	Dispersable
Ionic Nature	Non-ionic	Non-ionic	Non-ionic
% Actives	100	100	100
Density	1.06	1.027	1.02
Flash Point <sup>a</sup>	175° F.	230° F.	285° F.
Freezing Point	-9.4° F.	< 32° F.	< 32° F.
Molecular Weight	Copolymer	Copolymer	Copolymer

5

▪ Pensky-Martens closed cup ASTM D-93.

According to OSi's product bulletin, the following non-aqueous diluents have been found useful:

- ethylene-propylene oxide polymers (Ucon® 50HB
- 10 100, Union Carbide)
- methylester (Emery® 2235, Henkel)
- methylester (Emerest® 2301, Henkel)
- methylester (Emery® 2231, Henkel)
- propylene carbonate (Arco)
- 15 oleyl alcohol (Novol, Croda)

When preparing aqueous solutions or dispersions with these materials, OSi recommends pouring the silicone into the vortex of the total water while mixing at a moderate speed (about 300 rpm to about 400 rpm). Mixing is

20 continued until a uniform solution or dispersion is obtained. Non-aqueous solutions or dispersions are prepared in a similar manner, but mix at about 150 rpm to about 200 rpm until a clear mixture is obtained.

U.S. Pat. Nos. 4,690,955 (Kilgour et al.);

25 4,769,174 (Kilgour); 4,847,398 (Mehta et al.) and 4,857,583 (Austin et al.), disclose various organo-modified polysiloxane copolymers (i.e., organo-modified silicones) and methods of making same. Such copolymers contain hydroxyl groups. The amino-modification may be

30 performed by first substituting a halide for the hydroxyl group. The halide may then be reacted with ammonia or an amine to substitute an amino group for the halide. This latter process is called ammonolysis of halides. Alternatively, amino-modified polysiloxanes (i.e., amino-

35 modified silicones) may be prepared according to U.S. Pat. No. 3,905,823 (Piskoti), which is hereby incorporated by reference. Therein the amino-modified polysiloxanes are prepared by mixing an organo-modified polysiloxane (i.e., organo-modified silicone) with amino-

40 functional silanes or siloxanes and thereafter

5 equilibrating the mixture in the presence of a base catalyst, e.g., alkali metal hydroxides, alkoxides, hydrides, alkyls, alkenyls and aryls, and silanoates.

The modified silicone is generally used in the form of a solution, such as an aqueous solution containing at  
10 least 0.05% by weight up to, for example, 5% by weight of the modified silicone.

The lubricant composition need not coat the wearer-contacting surface completely. It is only necessary that enough lubricant composition is applied to enhance damp  
15 slip. It is preferred, to the extent that it is practicable, to keep the lubricant composition on the wearer-contacting surface, in the case of medical or dental gloves, in order to ensure that maximum grip is maintained on the outer surface. The lubricant  
20 composition can be applied as an aqueous solution containing from about 0.2 to about 2% by weight lubricant composition total. The article can be dipped in such solution or the solution can be sprayed or painted on it, preferably before it is removed from the form.  
25 Alternatively, the lubricant composition can be applied after the article is stripped from the form.

It is understood that other substrate polymers in dispersed, e.g., latex, form, including polyurethanes, may not need to be vulcanized like a natural rubber latex  
30 in every case, as can be readily appreciated by those skilled in the art.

It also is understood that various optional ingredients may be incorporated in these articles as apparent to those skilled in the art. For example, where  
35 the article is a glove, an antiblock agent may be used which would facilitate donning and use. The antiblock agent is preferably a low-melting wax (mp. from about 100° C. to about 150° C.) such as polyethylene wax added as an aqueous emulsion (e.g., 1-2%) to the coating

5 mixture. The particle size of the wax should be preferably less than 1  $\mu\text{m}$  to avoid interference with the surface morphology. Alternatively, anti-blocking agents may be micronized polyethylene or polytetrafluoroethylene.

10 In accordance with the present invention, an embodiment of a continuous process for making a powder-free glove comprises in summary form:

- (i) dip-coating a coagulant onto a glove form;
- (ii) dip-coating over the coagulant layer a layer of  
15 an elastomer;
- (iii) leaching the elastomer article in the hot water;
- (iv) priming the elastomer surface of the article while on the glove form, for example, by means  
20 of a dilute acid;
- (v) rinsing the primed surface in water or aqueous alkali;
- (vi) dipping the article, while still on the glove form, in an acrylic-type polymer dispersion and  
25 a curing agent therefor;
- (vii) heat curing the elastomer and polymer;
- (viii) removing the glove from the form, thereby reversing the glove (optional);
- (ix) chlorinating the glove;
- 30 (x) neutralizing the glove and residual chlorine;
- (xi) rinsing the glove;
- (xii) (optionally) treating the glove with a lubricant composition;
- (xiii) (accordingly optionally) drying the lubricant  
35 treated glove; and
- (xiv) removing the glove from the form, thereby reversing the glove (if step (viii) not used).

5           If the elastomer is not to be chlorinated, steps  
(ix) and(x) can be omitted.

          The application of the lubricant solution provides  
the chlorinated powder-free glove with superior lubricity  
with respect to wet/damp hand donning.

10           In an expanded manner, the steps for one embodiment  
of the present invention are discussed below. First  
there is a cleaning step to clean for example the hand  
form, typically made of porcelain, to remove residue from  
previous manufacturing iterations. The clean form is  
15 then dried to remove water residue by conveying the form  
through a preheated oven to evaporate the water.

          The preheated form is then dip-coated in a bath  
containing a coagulant, a powder source and a surfactant.

          The coagulant preferably contains calcium ions to break  
20 the protection system of the emulsion, thereby allowing  
the latex to deposit on the form. The powder is  
preferably a calcium carbonate powder which later acts as  
a release agent. Alternatively, the powder source may be  
omitted by using the lipo compound and surfactant  
25 combination in the coagulant to aid in stripping the  
glove according to U.S. Pat. No. 4,310,928 to Joung. The  
surfactant provides good wetting to avoid forming a  
meniscus and trapping air between the form and deposited  
latex, particularly in the cuff area. An example of such  
30 a surfactant is an acetylene diol. As noted above, the  
form has been preheated in the drying step and the  
residual heat dries off the water leaving calcium  
nitrate, calcium carbonate powder and surfactant on the  
surface of the form.

35           The coated form is then dipped into a latex  
containing tank. The latex contains for example, natural  
rubber latex plus stabilizers, antioxidant, activators,  
accelerators, and vulcanizers, and the latter all being  
in powder form. The stabilizers are preferably of the  
40 phosphate type surfactants. The antioxidants are

5 preferably the phenol type, for example, Antioxidant 2246<sup>7</sup>  
(2,2'-methylenebis (4-methyl-6-t-butylphenol)) available  
from PMC Specialty Group, Fords, NJ. The activator may  
be for example zinc oxide. The accelerator may be for  
example dithiocarbamate. The vulcanizer is preferably  
10 sulphur or a sulphur-containing compound. If these  
materials are used, the stabilizer, antioxidant,  
activator, accelerator and vulcanizer are dispersed into  
water to avoid crumb formation by using a ball mill or an  
attritor. This dispersion is then mixed into the latex.  
15 An emulsified wax, which is used as an antiozonant, is  
then added to the latex mixture. The coated form is then  
dipped into the latex composition with the thickness of  
the latex deposited thereon controlled by the duration of  
the dip (in a single dip situation). This is about 5 to  
20 about 20 seconds, e.g., about 12 seconds, for a surgical  
glove; and about 20 to about 70 seconds, e.g., about  
50 seconds, for an orthopedic glove.

The form now coated with latex is then dipped into a  
leaching tank in which hot water is circulated to leach  
25 out all water soluble components for example residual  
calcium nitrates and proteins contained in the natural  
latex. This leaching process may continue for about  
twelve minutes with the tank water being about 120° F.

The form is then dipped into a tank containing the  
30 acrylic-type resin dispersion containing the curing agent  
with the thickness of the latex deposited thereon  
controlled by the duration of the dip (in a single dip  
situation).

The form is then extracted from the coating tank to  
35 a bead and print station. At this station, a bead is  
formed around the cuff area at the end of the glove by  
mechanically rolling down the top portion or the end  
portion of the glove a predetermined amount. Company  
logos, size and a traceable date of manufacture are then

5 printed onto the exterior of the glove, for example by  
injecting ink into the latex coating on the form.

The latex/polymer coated form is then sent to a curing station where the natural rubber in the form substrate coating is vulcanized and the polymer is cured  
10 typically in an oven, thereby heat curing the rubber and curing the acrylic-type resin. The curing station initially evaporates any remaining water in the coating of the form and then proceeds to the higher temperature vulcanization of the rubber and curing of the acrylic-  
15 type resin. The drying may occur between 190° F. to 200° F. with a vulcanization step occurring at temperatures for example from about 220° F. to about 240° F. This overall process may last about forty to forty-five minutes total. For example, the oven may be  
20 divided into four different zones with a form being conveyed through the zones of increasing temperature. One example is an oven having four zones with the first two zones being dedicated to drying and the second two zones being primarily the vulcanization step. Each of  
25 the zones may have a slightly higher temperature, for example, the first zone at about 180° F., the second zone at about 200° F., a third zone at about 220° F. and a final zone at about 240° F. The residence time of the form within a zone in this case is about ten minutes or  
30 so. The accelerator and vulcanizer contained in the latex coating of the form are used to cross-link the natural rubber therein. The vulcanizer forms sulphur bridges between different rubber segments and the accelerator is used to speed up sulphur bridge formation.  
35 The resin is crosslinked and covalently bonded to the rubber substrate.

The gloves may be removed from the glove forms and then chlorinated or chlorinated while on the forms. If a



5 continuous process is used, the cured gloves leaving the  
curing station and optionally still on the form are then  
chlorinated. The chlorination, or more generally  
halogenation, may be performed in any suitable manner  
known to those skilled in the art. Such methods include  
10 (1) direct injection of chlorine gas into the water  
mixture, (2) mixing high density bleaching powder and  
aluminum chloride in water, (3) brine electrolysis to  
produce chlorinated water, and (4) acidified bleach.  
See for example U.S. Pat. Nos. 3,411,982 (Kavalir),  
15 3,740,262 (Agostinelli), 3,992,221 (Homsy, et al.;  
however, it is modified to treat the wearer-contacting  
surface rather than or in addition to treating outer  
surface with chlorine gas), 4,597,108 (Momose), and  
4,851,266 (Momose). One preferred method is to inject  
20 chlorine gas into a water stream and then feed the  
chlorinated water into a chlorinator (a closed vessel)  
containing the washed gloves. The concentration of  
chlorine can be monitored and controlled to control the  
degree of chlorination. The chlorine concentration is  
25 typically at least about 500 ppm, preferably from about  
500 ppm to about 1,200 ppm, e.g., about 800 ppm. The  
time duration of the chlorination step may also be  
controlled to control the degree of chlorination. The  
time duration may range from about 3 to about 20 minutes,  
30 e.g., 7 minutes. The gloves being in a collapsed state  
will chlorinate to a greater extent on the outside  
surface with a lesser amount on the inside surface of the  
glove.

In another preferred method, the gloves (removed  
35 from the forms) may be chlorinated by placing them into a  
chlorinator, including a front-loaded industrial washer,  
containing a water bath which contains bleach which is  
subsequently acidified to a pH of 2 to about 3. The  
chlorine concentration ranges from about 0.05 to about  
40 0.3 wt.%, e.g., about 0.1 wt.%. The time duration ranges

5 from about 3 to about 25 minutes. Again, the outside  
surface of the glove will have a greater amount of  
chlorination than the inside surface of the glove. The  
degree of chlorination of the inner and outer surfaces of  
the glove can be controlled by choosing which side of the  
10 glove is on the outside or by repeating the chlorination  
step or a combination of both inversions of the glove and  
repeated chlorination.

The acidified bleach is then neutralized preferably  
with ammonium hydroxide or with sodium thiosulfate. This  
15 step neutralizes the acidified water contained in the  
chlorinator and quenches excess chlorine to ammonium  
chloride, if ammonium hydroxide is used.

Still within the industrial washer, the chlorinated  
gloves are then rinsed with tap water at about ambient  
20 temperature. This rinse cycle may be repeated as  
necessary. Once all water is removed from the front-load  
washer, the gloves are tumbled to drain excess water.

A lubricant solution is then added into the  
chlorinator containing gloves which are then tumbled for  
25 about five minutes. This coats the outside of the glove  
with the lubricant solution. The lubricant solution is  
drained from the chlorinator and may be reused. If  
reused, the lubricant solution is preferably reused once  
more.

30 The coated gloves are then put into a drier and  
dried for about ten to fifteen minutes at about 110° F. to  
dry the donning surface. The gloves are then reinverted  
and dried for about twenty-five minutes at about 120° F.  
The foregoing shows a sequence of events in the  
35 manufacture of gloves according to the present invention.

5 **EXAMPLES**

To further the understanding of the invention the following examples are provided as a means of illustration.

10 **EXAMPLE 1:**

A surgical glove was processed by submerging the hot form in coagulant, immersing it in a natural rubber latex, leaching it in tap water, acid pretreatment with a two percent sulfuric acid solution, and then overdipping with a solution containing an acrylic latex (Rohm and Haas AC-1024), a melamine crosslinker such as Cymel 303 or Cymel 373,  $\text{Al}(\text{NO}_3)_3$  (a metal salt), and phosphoric acid as an acid catalyst. The coated forms were placed in an oven for 30 minutes at  $110^\circ\text{C}$ . The gloves were stripped from the formers and washed with water to remove any particulate material and thoroughly dried. In this example, the gloves were not halogenated. A scale from 1-5 was used to rank the donning performance of the articles generated from Formulations 1-5 where:

25 **Table 1**

Rating	Explanation
1	Tacky; glove difficult to start to don
2	Poor; glove tends to adhere to hand
3	Fair; glove goes on with moderate effort
4	Good; donning with some dress down
5	Excellent; donning with no dress down

In each of the following formulations, the ingredients were added in the following order slowly agitating throughout the process. The aluminum nitrate  
30  $(\text{Al}(\text{NO}_3)_3)$  was put into the water and agitated until dissolved. The melamine crosslinker (Cymel 303 or

5 Cymel 373) were added to the solution with agitation until dissolved. The resin and phosphoric acid were then added.

	<u>Formulation</u> <u>Number</u>	<u>Composition (Weight</u> <u>Percentage)</u>	<u>Dry Skin</u> <u>Slip</u>
10	1	Al(NO <sub>3</sub> ) <sub>3</sub> = .95% Rohm & Haas AC-1024 = 15.15% Cymel® 303 = 2.67% Phosphoric Acid = 0.07% Water = 81.17%	5
15			
20	2	Al(NO <sub>3</sub> ) <sub>3</sub> = 1.03% Rohm & Haas TR-520 = 15.15% Cymel® 303 = 2.67% Phosphoric Acid = 0.07% Water = 81.08%	5
25	3	Al(NO <sub>3</sub> ) <sub>3</sub> = 1.01% Rohm & Haas E-32NP = 15.15% Cymel® 303 = 2.67% Phosphoric Acid = 0.07% Water = 81.08%	5
30	4	Al(NO <sub>3</sub> ) <sub>3</sub> = 1.04% Rohm & Haas AC-1024 = 15.15% Cymel® 373 = 2.67% Phosphoric Acid = 0.04% Water = 81.08%	5
35			
40	5	Al(NO <sub>3</sub> ) <sub>3</sub> = 1.01% Rohm & Haas TR-520 = 15.15% Cymel® 303 = 2.67% Phosphoric Acid = 0.07% Water = 81.08%	5

5

EXAMPLE 2:

Gloves from Formulation 1 in Example 1 were removed from the form after cooling, washed with water, chlorinated, and then treated with a combination of slip agents. The gloves produced were essentially free of powder, non-blocking, soft, and exhibited excellent adhesion up to the break elongation point of the base natural rubber elastomer. The gloves were also found to exhibit good damp and dry slip. In this example, chlorination of the elastomeric articles was performed using the steps of:

(a) rinsing all particulate matter from six coated elastomeric articles with water,

(b) placing the elastomeric articles into a suitable corrosion-resistant container,

(c) adding about 2000 mL water into the container and adding about 12.4 grams of 8.5% active bleach,

(d) agitating the elastomeric articles for about five minutes and subsequently injecting about five grams of concentrated hydrochloric acid,

(e) agitating for about ten minutes more,

(f) adding about twenty grams of 37% ammonium hydroxide and agitate for about five minutes more,

(g) rinsing the gloves thoroughly with water before being immersed and tumbled in a suitable combination of slip agents, and then

- 5 (h) tumbling the gloves in a dryer until dry.

Gloves prepared in Example 1 were chlorinated and post-treated with various compositions of slip agents and evaluated with respect to damp skin. The following post-treated gloves from Example 1 were prepared and evaluated  
 10 for donning with respect to damp. The results of these evaluations are summarized in Tables 2 through 5 (when "%" means weight percent).

Three (3) pairs of gloves were tested for each sample, with each pair donned by a different member of a  
 15 three-person panel.

Table 2

Sample	CPC	N-500	Damp Skin Lubricity <sup>a</sup>
1	1.0%	0.75%	3/4/4
2	0.50%	0.50%	2/3/4
3	0.25%	0.50%	3/4/4
4	2.00%	1.00%	3/5/4
5	0.50%	0.10%	5/4/4

a) first/second/third person's rating.

Table 3

Sample	CPC & BAC	N-500	Damp Skin Lubricity
6	0.50% & 0.25%	0.25%	5/3/4/5
7	0.00% & 0.50%	0.50%	2/2/2
8	0.25% & 1.00%	0.25%	4/4/3
9	0.25% & 1.00%	0.50%	4/3/4
10	0.25% & 0.75%	0.50%	5/5/3

5 Table 4

Sample	CPC & BAC	N-300	Damp Skin Lubricity
11	0.50% & 0.25%	0.25%	3/4/3
12	0.00% & 0.50%	0.50%	2/3/2
13	0.25% & 1.00%	0.25%	3/2/2
14	0.25% & 1.00%	0.50%	3/4/3
15	0.25% & 0.75%	0.50%	3/3/3

Table 5

Sample	CPC and PEO	N-500	Damp Skin Lubricity
16	1.0% & 1.0%	0.75%	3/5/3
17	0.50% & 1.0%	0.50%	2/4/3
18	0.25% & 1.0%	0.50%	4/2/4
19	2.00% & 1.0%	1.00%	4/3/3
20	0.50% & 1.0%	0.10%	4/4/4

5 EXAMPLE 3:

In this example, the following ingredients were added in the following order to prepare the resin coating bath composition using slow agitation throughout the preparation process. About 140.67 grams of aluminum  
10 nitrate ( $\text{Al}(\text{NO}_3)_3$ ) was added to about 15,360.24 grams of water. These ingredients were agitated until all the aluminum nitrate went into solution. Then, about 132.08 grams of Cymel® 350 crosslinker was added to the solution and agitated until it went into solution. Thereafter,  
15 about 2,526.02 grams of Rohm and Haas Rhoplex® AC-1024 resin and about 9.58 grams of phosphoric acid (85% v/v) were added forming the resin coating bath solution.

Resin coated surgical gloves were made in the same manner as in Example 1, except that the foregoing resin  
20 solution was used instead. The coated gloves were then chlorinated according to Example 2. The gloves were then treated with a variety of lubricant compositions each of which was a mixture of a silicone surfactant and at least one organic surfactant. The resulting gloves were then  
25 tested for damp donning and rated using the rating system identified in Example 1. The results are given in Table 6, with Table 7 providing a description of the various surfactants used and others that may also be suitable for use in the present invention. In this  
30 example, the samples that exhibited the best donning damp and dry slip for those having a lubricant composition of CPC with DC 365 and CPC with Silwet® L-7001.



5

Table 6

Sample	Silicone Surfactant	Organic Surfactant	Damp Skin Lubricity
21	0.25 % DC 365	0.5% CPC	4-5
22	0.1 % DC 365	0.5% CPC	4-5
23	0.25 % L-7001	0.5% CPC/ 0.1% Patioinic SSL	4
24	0.1 % L-7001	0.5% CPC	4-5
25	0.25 % L-7605	0.5 % Witco VTSC	4
26	0.5 % L-7001	0.5% CPC	4-5
27	1.0 % L-7001	0.5% CPC	4-5
28	0.25 % L-7605	0.5 % K5721	4
29	0.25 % L-7001	0.5% CPC	4-5
30	0.25 % L-7605	0.5% CPC	4-5
31	0.25 % L-7605	0.5% E6075	4
32	0.25 % L-7001	0.5% GLG-7	4
33	0.25 % L-7001	0.5% F160	4
34	0.25 % L-7001	0.5% Mack 007	3

35	0.25 % L-7001	0.5% Crodafos N10	4-5
36	0.25 % L-7001	0.5% Detain PB	3-4
37	0.25 % L-7001	0.5% P188C	4
38	0.25 % L-7001	0.25% CPC/ 0.25% Pationic SSL	4
39	0.25% N-300	0.5 % Mack 426	4
40	0.25% N-300	0.75 % Mack 426	4
41	0.25% N-300	2.0 % Mack 426	4
42	0.1% N-300	0.5 % CTMAC	4
43	0.25% N-300	0.75 % Mackom	4
44	0.25% N-300	0.5% Mackom	4
45	0.25 % L-7001	0.5 % P122A	4
46	0.25 % L-7001	0.5 % Crodafos N3	4
47	0.25 % L-7001	0.5 % CPC	4-5
48	0.25 % L-7001	0.5 % CPC	4-5
49	0.25 % L-7001	1.0% CTMAC	3-4
50	0.5 % DC 365	0.3 % CPC/ 0.2 % PSSSL	3-4
51	0.25 % DC 365	0.3 % CPC/ 0.2 % PSSSL	4-5

5 Table 7

## Listing of Post Processing Slip Ingredients Evaluated

Product Designation	Product Type	Manufacturer	Composition
Ritasil® 190	Polyethersiloxane	RITA Corp.	Dimethicone
Ritasil® 193	Polyethersiloxane	RITA Corp.	Dimethicone
NuWet® 300	Aminomodified silicone-polyether copolymer	OSi Specialities	Silicone Polyether
NuWet® 500	Organomodified Polydimethylsiloxane	OSi Specialities	Polydimethylsiloxane/ Ethoxylated Alkyl Blend
Silwet® L-7001	Silicone Copolymer	OSi Specialities	Silicone Polyether
Silwet® L-7605	Silicone Copolymer	OSi Specialities	Silicone Copolymer
Dow Corning® DC 365	Aminofunctional Siloxane emulsion	Dow Corning	Dimethylsilyl Dimethyl-aminoethyl - aminopropyl Silicone
Witcosoft® 110	Cationic Surfactant	Witco	Methyl-bis Hydrogenated Tallow Amidoethyl-Ammonium Methyl Sulfate

5 Table 7 - Continued

Witcosoft® 222 LT90	Cationic Surfactant	Witco	Methyl bis(alkylamido ethyl) 2- Hydroxyethyl Ammonium Methyl Sulfate, Ethoxylated
Witcosoft® 222 PG	Cationic Surfactant	Witco	Methyl Bis (Tallow Amido Ethyl) 2- Hydroxyethyl Ammonium Methyl Sulfate
Witcosoft® 315	Cationic Surfactant	Witco	Dimethyl Dialkyl (C14- 18) Ammonium Chloride
Varisoft® BT85	Quaternary Ammonium Compounds	Witco	Trimethyl Ammonium Chloride
Varisoft® CSAC	Cationic Surfactants, surfactant blends	Witco	Benzenemethana min-ium, N,N- Dimethyl-N- Octadecyl- Chloride and Ethoxylated Castor Oil
Varisoft® TSC (VTSC)	Quaternary Ammonium Compounds	Witco	Stearyl Trimethyl Ammonium Chloride
Varisoft ® 442 100P	Quaternary Ammonium Compounds	Witco	Quaternium-18; Dimethyl Di - hydrogenated Tallow Ammonium Chloride

5 Table 7 - Continued

Varox® 1770	Nonionics	Witco	Cocamidopropyl amine Oxide
Emcol® E6075	Quaternary Ammonium Compounds	Witco	N(Stearoyl Colamine Formyl Methyl) Pyridinium Chloride
Kemester® 5721	Fatty Acid Ester, Nonionics	Witco	Tridecyl Stearate
Witconol® 2720	Polysorbate 20, Nonionics	Witco	No data available
Witcodet® 804	Mixture of Surfactants	Witco	No data available
Miranol® Ultra C32	Organic Surfactant	Rhone- Poulenc	Sodium Cocoamphoaceta te
Geropon® 99	Organic Surfactant	Rhone- Poulenc	Sodium Dioctyl Sulfosuccinate
Mackanate® OM (Mackem)	Organic Surfactant	McIntyre Group	Disodium Solfosuccinate
Rhodafac® RA- 600	Complex Organic Phosphate Esters	Rhone- Poulenc	Poly(Oxy-1- ethanediyl), Alpha-Hydro- Omega-Hydroxy- , C8-10 alkyl ethers, Phosphate
Crodesta® F- 160	Carbohydrate Fatty Ester	Croda	Sucrose Stearate

5

Crodafos® N10	Alkoxy Ether Phosphate, Amine Salt	Croda	Polyoxy-ethylene (10) Oleyl Ether Phosphate, Amine Salt
Crodafos® N3 Neutral	Alkoxy Ether Phosphate, Amine Salt	Croda	Polyoxy-ethylene (3) Oleyl Ether Phosphate, Diethanolamine Salt
Mackalene® 426	Cationic Surfactant	McIntyre Group Inc.	Isostearamidopropyl Morpholine Lactate
Pationic® 122A (PIZZA)	Lactylate	R.I.T.A. Corp.	Sodium Caproyl Lactylate
Pationic® 138C (P138C)	Lactylate	R.I.T.A. Corp	Sodium Lauroyl Lactylate
Pationic® SSL	Lactylate	R.I.T.A. Corp	Sodium Stearoyl Lactylate
Tergitol® NP-9	Nonionic	Union Carbide	Nonyl Phenol Ethoxylate
Cetyl Pyridinium Chloride	Quaternary	Spectrum Chemical	Cetyl Pyridinium Chloride
Pationic® CSL	Lactylate	R.I.T.A. Corp	Calcium Stearoyl Lactylate
Benzalkonium Chloride	Cationic	Aldrich	Benzalkonium Chloride
Cetyl Trimethyl-ammonium Chloride (CTMAC)	Cationic	Aldrich	Cetyl Trimethyl-ammonium Chloride
Poly Ox® 205	Polyethylene Oxide	Union Carbide	Polyethylene Oxide

Detain® PB	Betaine	Deforest Products	Betaine
Crodafos® N-3	Phosphate Esters	Croda	DEA Oleth-3 Phosphate
Arcol® 11-34	Polyoxypro- pylene ether glycol	Arco	6000 m.w. Polypropylene Ether Glycol
Mac® k 007	Polyquat	McIntyre	Polyquaterium- 7

5

In Tables 2 through 6, the abbreviations have the following meaning:

Abbreviation	Explanation
CPC	cetylpyridinium chloride
BAC	benzalkonium chloride
N-500	NuWet® 500
N-300	NuWet® 300
PEO	Polyethyleneoxide

#### Example 4

10 In accordance with EXAMPLE 1, a glove was produced by dipping the prepared natural rubber latex layer with the following overdip compositions (i.e., the resin coating both composition). This example involved styrene acrylic lattices with urea-formaldehyde or glycoluridil crosslinkers. The only difference from Example 1 was that  
15 no acid was used in the leach or as a predip to prepare the natural rubber latex surface. Rather, the acid was included in the formulation itself, thereby eliminating the separate acid step.

20 In the following formulations, the ingredients were added in the following order to prepare the resin coating bath composition using slow agitation throughout the preparation process. The aluminum nitrate (when present) was added to the water and the mixture agitated until the  
25 aluminum nitrate went into solution. Then, the crosslinker (e.g., Beetle® 65, Cymel® 1171 or Cymel® 1172) was added to the solution and agitated until it went into solution. Thereafter, the resin (Rohm and Haas Rhoplex® AC-3094, AC-1024 or AC-2573) and the acid  
30 catalyst (Cycat® 4040) were added and agitated. Then the sulfuric acid was added for treating the surface of the natural rubber latex to enhance the covalent bonding of the resin coating to the latex substrate once tiered.



5

## FORMULATION 6

Rohm & Haas AC-3094- 68.16 grams  
Beetle® 65- 12 grams.  
10 Cycat® 4040- 0.3 grams  
Aluminum Nitrate- 4.26 grams  
Sulfuric Acid- 0.45 grams  
Water- 565.18 grams

15

## FORMULATION 7

Rohm and Haas AC-1024- 68.16 grams  
Beetle® 65- 6 grams  
Cycat® 4040- 0.3 grams  
20 Sulfuric Acid- 0.9 grams  
Aluminum Nitrate- 4.26 grams  
Water- 666.66 grams

## FORMULATION 8

25

Rohm and Haas AC-2573- 616.78 grams  
Cymel® 1171- 108.59 grams  
Water- 5,114.36 grams  
Cycat® 4040- 5.00 grams  
30 Sulfuric Acid- 20.01 grams

## FORMULATION 9

Rohm and Haas AC-2573- 616.78 grams  
35 Cymel® 1172- 108.59 grams  
Water- 5,114.36 grams  
Cycat® 4040- 5.00 grams  
Sulfuric Acid- 20.00 grams

40

The elastomeric articles prepared with  
formulations 6 through 9 above were chlorinated according  
to Example 2 and treated with a composition of slip  
agents. The resulting elastomeric articles were soft and  
45 exhibited excellent adhesion of the coating even up until  
break elongation of the base neoprene elastomer. The  
powderfree post-treated elastomers were non-blocking and  
exhibited excellent lubricity with respect to damp and  
dry skin.

50

5 **EXAMPLE 5**

In accordance with the general procedure of Example 1, Example 5 involved the overcoating of neoprene lattices with acrylic lattices crosslinked with melamines. The neoprene latex formulations were prepared from commercial emulsions such as DuPont Dow Elastomers 671A, 750, and 571. The neoprene (i.e., polychloroprene) latexes were compounded with additives including zinc oxide, thixotropes according to Table 8 with preferred ranges for suitable formulations identified within parenthesis.

The neoprene latex used in the example had the following components:

Table 8

COMPONENTS	PARTS BY WEIGHT (PREFERRED RANGE)
DuPONT NEOPRENE LATEX 571 (chlorinated rubber latex emulsion)	100 (40 TO 150)
DARVAN® SMO (monosodium salt of sulfated methyl oleate)	3 (1 TO 10)
DARVAN® WAQ (sodium lauryl sulfate)	1 ( 0.2 TO 5)
ZINC OXIDE curative (crosslinker)	5 (1 TO 20)
Antioxidant (Sustane)	2 (1 TO 10)
McNAMEE® CLAY kaolin (thixotrope)	10 (2 TO 20)
ETHYL TUADS accelerator (tetraethylthiuram disulfide)	1 (0.2 TO 5)
BUTYL NAMATE (sodium dibutyl dithiocarbamate) latex accelerator	1 (0.2 TO 5)

20

A number of other commercial polychloroprene latexes may be used including preferably Neoprene Latexes 671 and 750 also available from DuPont, the formulation above is representative.

25

An acid treatment step was included as a separate step with the neoprene lattices. The neoprene coated form was submerged in a solution containing two percent sulfuric acid for a period of sixty seconds prior to overcoating with the styrene-acrylic solutions. The coating solutions employed in the invention are detailed

30

5 below.

#### FORMULATION 10

10 Rohm and Haas AC-2573- 76.50 grams  
Cymel® 303- 5.60 grams  
Water- 465.18 grams  
Phosphoric Acid- 0.29 grams

#### FORMULATION 11

15 Rohm and Haas AC-1024- 76.50 grams  
Cymel® 303- 5.60 grams  
Water- 465.18 grams  
Phosphoric Acid- 0.29 grams

20 Formulation 10 was chlorinated and treated with an aqueous surfactant of 0.5% cetylpyridinium chloride and 0.25% dimethicone. Formulation 11 was chlorinated and also treated with an aqueous solution of dimethicone. The elastomeric articles were soft and exhibited excellent adhesion of the coating even up until break elongation of  
25 the base neoprene elastomer. The powderfree post-treated elastomers were non-blocking and exhibited excellent lubricity with respect to damp and dry skin.

The present invention has been described primarily with respect to surgeon's gloves. As earlier noted, the  
30 present invention is also applicable to other skin- or tissue-contacting flexible elastomeric articles, such as condoms, gloves used by doctors and veterinary surgeons for examination purposes (such gloves often being donned with dry hands), catheters, ureters, sheets, sheaths and  
35 sheath-type incontinence device.

When the present invention is used for articles such as ureters and catheters, the outer surface is coated with the lubricant composition (this being the wearer-contacting surface); for condoms the inner and/or outer  
40 surface may be treated with the lubricant composition.

5 WHAT IS CLAIMED IS:

1. A method of treating an elastomeric flexible article, the method comprising:

coating the article surface with an acrylic-type  
10 resin which contains styrene;

curing the resin coating;

halogenating at least one surface of the article;

neutralizing the article surface and residual  
chlorine; and

15 treating the article surface with a lubricant composition,

wherein the lubricant composition is selected from the group consisting of a first composition and a second composition,

20 wherein the first composition comprises

an acetylenic diol and

at least one compound selected from the group consisting of

an organo-modified silicone,

25 an amino-modified silicone, and

a cationic surfactant, and

wherein the second composition comprises

a cationic surfactant and

at least one compound selected from the group  
30 consisting of

an organo-modified silicone,

an amino-modified silicone, and

an acetylenic diol.

35 2. A method according to claim 1, wherein the cationic surfactant is 1-hexadecylpyridinium chloride monohydrate.

- 5           3.    A flexible elastomeric article having a wearer-  
              contacting surface in which a lubricant composition has  
              been applied to the wearer-contacting surface so as to  
              substantially improve the lubricity of the surface with  
              respect to damp skin, wherein the lubricant composition  
10    is selected from the group consisting of a first  
              composition and a second composition,  
              wherein the first composition comprises  
                  an acetylenic diol and  
                  at least one compound selected from the group  
15    consisting of  
                  an organo-modified silicone,  
                  an amino-modified silicone, and  
                  a cationic surfactant, and  
              wherein the second composition comprises  
20               a cationic surfactant and  
                  at least one compound selected from the group  
              consisting of  
                  an organo-modified silicone,  
                  an amino-modified silicone, and  
25               an acetylenic diol.
4.    An article according to claim 4, wherein the  
              article is a surgeon's glove.
- 30           5.    An article according to claim 4, wherein the  
              cationic surfactant is 1-hexadecylpyridinium chloride  
              monohydrate.

5

6. A flexible article displaying slip properties with respect to damp and dry mammalian tissue without use of powder lubricants comprising:

10 a substrate layer comprising an elastomeric material, the layer having a wearer-contacting surface; and

15 a damp slip-conferring amount of a lubricant composition applied to the wearer-contacting surface, wherein the lubricant composition is selected from the group consisting of a first composition and a second composition,

wherein the first composition comprises  
an acetylenic diol and  
at least one compound selected from the group  
20 consisting of

an organo-modified silicone,  
an amino-modified silicone, and  
a cationic surfactant, and

wherein the second composition comprises  
25 a cationic surfactant and  
at least one compound selected from the group consisting of

30 an organo-modified silicone,  
an amino-modified silicone, and  
an acetylenic diol.

7. An article according to claim 7, wherein the article is a surgeon's glove.

35 8. An article according to claim 7, wherein the cationic surfactant is 1-hexadecylpyridinium chloride monohydrate.

5           9. An article according to claim 7, wherein the  
elastomer is selected from the group consisting of  
natural rubber, a polyurethane, a homopolymer of a  
conjugated diene, a copolymer of at least two conjugated  
dienes, a copolymer of at least one conjugated diene and  
10 at least one vinyl monomer, and combinations thereof.

10. An article according to claim 10, wherein the  
elastomer is natural rubber.

15           11. An article according to claim 10, wherein the  
elastomer is a polyurethane.

12. An article according to claim 10, wherein the  
article has a first elastomeric layer and a second  
20 elastomeric layer and wherein the elastomer for the first  
elastomeric layer is natural rubber and the elastomer for  
the second elastomeric layer is polyurethane.

13. An article according to claim 10, wherein the  
25 elastomer is a homopolymer of a conjugated diene.

14. An article according to claim 14, wherein the  
elastomer is neoprene.

30           15. An article according to claim 14, wherein the  
conjugated diene is isoprene.

16. An article according to claim 10, wherein the  
elastomer is a copolymer of at least one conjugated diene  
35 and at least one vinyl monomer.

17. An article according to claim 17, wherein the  
elastomer is nitrile rubber.

5        18. An article according to claim 17, wherein the elastomer is a styrene-isoprene-styrene block copolymer.

19. An article according to claim 17, wherein the elastomer is a styrene-butadiene-styrene block copolymer.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/23777

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08J/04 A61L31/00 A61B19/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J A01N A41D A61B A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92 13497 A (SMITH & NEPHEW) 20 August 1992 see claims 1,2,6,7	3
A	EP 0 467 869 A (UNIV COLUMBIA) 22 January 1992 see claims 1,4,5 see example 1	3
A	EP 0 198 514 A (LRC PRODUCTS) 22 October 1986 cited in the application see claims 1,4,5	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Niaounakis, M

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